A Study of the Glow of Phosphorus.—Periodic Luminosity and Action of Inhibiting Substances.

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§ 1. *Introduction.*

Many experimenters who have used cold phosphorus for the absorption of oxygen from air must have noticed the appearance of flickering clouds of luminosity when the action is nearly complete. These occur in the gas space and obviously represent a delayed action between the slight oxygen residue and the vapour of phosphorus.* This action has been discussed by Joubert,† who recognised it as due to the propagation of combustion in an explosive mixture. He obtained it in a more striking form by the slow leakage of air into an exhausted vessel containing phosphorus: his conclusion was that below a certain pressure, too small to measure, phosphorus vapour would not combine with oxygen. As the mixture of phosphorus vapour and oxygen became richer in oxygen by the inflow of the latter, the point was reached when combustion became possible and an explosion was propagated.

From the point of view of kinetic theory it seemed very strange that phosphorus vapour should behave thus. Joubert's view of the facts would seem to imply that the reaction of a molecule of phosphorus with oxygen was not dependant solely on the character and energy of molecular collisions, but also on the absolute value of the interval of time between them. These theoretical difficulties, and also the fascination of the experiments themselves, led me to attempt a further investigation.

§ 2. *Travelling Pulses of Luminosity. Need for the Presence of Water.*

The earlier attempts were directed to getting the effect in as striking a form as possible. The first experiment which gave results worthy of record was as follows: A horizontal glass tube 48 cm. long and 2 cm. diameter (fig. 1) was closed at the ends. Along the top side, at intervals of about 4 cm. a number of lateral openings were provided, to each of which was attached a long vertical capillary tube about 1 mm. in diameter, and 1 metre long. These tubes were open at the far end to the air of the room. Along the bottom of the main horizontal tube was a layer of phosphorus. This had been melted into position under a layer of water. After cooling the water was poured off as far as possible. The lateral tubes were then attached as described. The phosphorus at first presented a uniform luminous surface where it glowed in contact with the contained air, but after a time when the oxygen began to approach exhaustion, a flickering appearance set in. This developed, as the action proceeded, into a very definite and distinctive form. At the side entrances air was diffusing into the nitrogen atmosphere, which contained phosphorus vapour. Luminous pulses were observed to spring into existence at these side entrances, to divide, and to travel in opposite directions along the tube. The pulses were of the same diameter as the tube (2 cm.) and in thickness less than 1 cm. Their rate of travel was estimated at between 1 and 2 cm. per second. When two pulses originating at different places met one another, both were destroyed. It is easy to see why this should be the case. Suppose for distinctness of statement that the phosphorus vapour is in excess. Then each pulse as it passes leaves the space behind it exhausted of oxygen—its passage may be compared to the passage of an army living on the country, or a flight of locusts—no supplies are left in the rear. Another pulse meeting the first finds no oxygen to support its further advance or existence.

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* In this paper I do not enter upon the question of whether the glow is due directly to oxidation of phosphorus, or of phosphorus trioxide. When, for brevity, the oxidation of phosphorus is referred to, this reservation should be understood.

† 'École Norm. Annales,' vol. 3, 1874, p. 209.

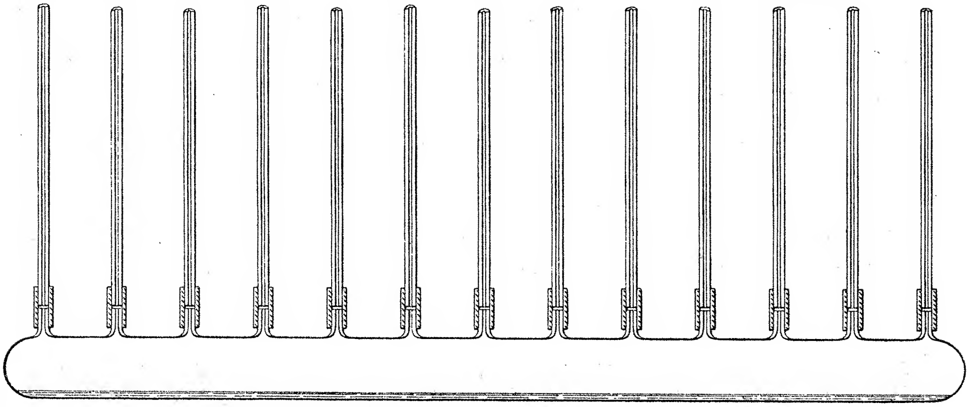

FIG. 1.

The arrangement of side entrances described was designed to provide, as far as possible, for a uniform admixture of phosphorus vapour and oxygen along the tube. On occasion a single pulse has been observed to traverse nearly the entire length. As a rule the pulses originated chiefly at two or three particular side junctions, perhaps owing to a favourable condition of the phosphorus surface for evaporation near these entrances; but the action was somewhat variable from day to day. A rise of the barometric pressure would cause oxygen to enter more rapidly than by diffusion, and a change of temperature also had some effect.

This apparatus continued to work well for a week or more, and was expected to do so almost indefinitely. But after a time it was noticed that the pulses were fewer and less brilliant, and that there were patches of stationary luminosity in the tube. After various possible explanations of the change had been examined, it was found to be due to the gradual drying of the phosphorus under the desiccating influence of the phosphorus pentoxide produced. On adding a few drops of water, the original condition was recovered.

For further examination of the effect of moisture, a tube was prepared, as in fig. 2, with a single side entrance, and a layer of phosphorus on the bottom. It was dried out by exhaustion on a mercury pump, with which a phosphorus pentoxide drying tube was connected. It was then filled up with commercial nitrogen (to save time), and the capillary entrance tube attached. There was now no trace whatever of the luminous travelling pulses. The glow, when air was entering, was perfectly steady, and took the form shown in fig. 2, *a*, *b*, *c*, which represent successive appearances as the air influx was gradually diminished. Any one of these stages could be maintained indefinitely.

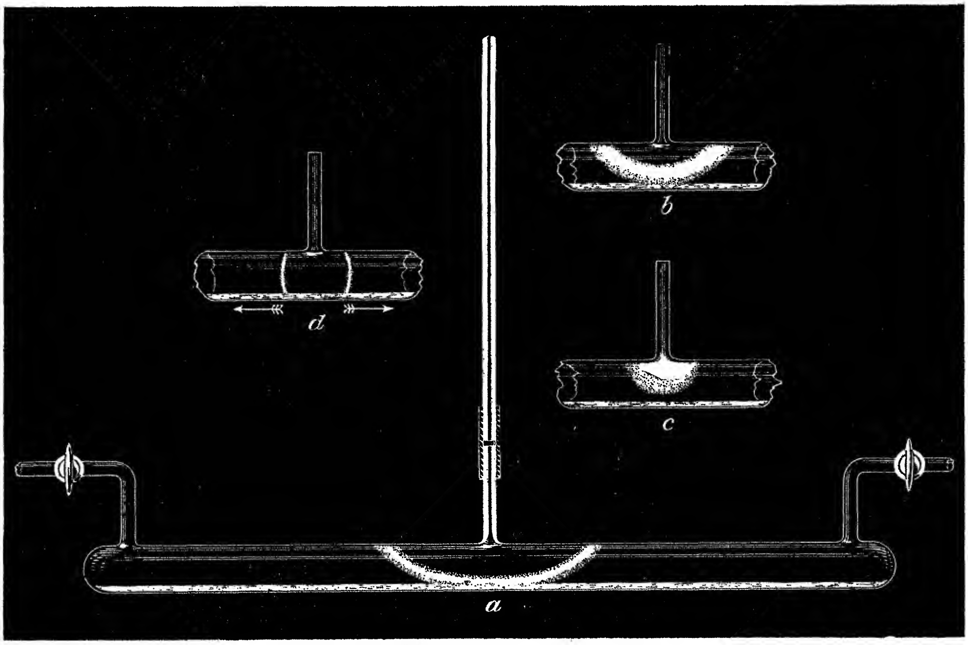

Fig. 2.

On adding a few drops of water, a constant succession of travelling pulses was substituted for the steady luminosity (fig. 2, *d*). In this case a pulse, starting from where the oxygen was most concentrated, divided, and travelled in each direction into a region where the oxygen became progressively scarcer. Thus the pulse gradually lost in intensity, and became extinguished after travelling a distance of perhaps 6 cm.

It is quite clear, then, that in these experiments the presence of water vapour is an essential condition for the periodic luminosity.

The quantity of water vapour necessary was next studied. In this case a tall narrow exhausted bottle was used, near the bottom of which was hung up a small piece of phosphorus—a slice cut from one of the ordinary commercial sticks. Air could be slowly admitted through a capillary tube, so as to raise the pressure a few millimetres per hour (fig. 3).

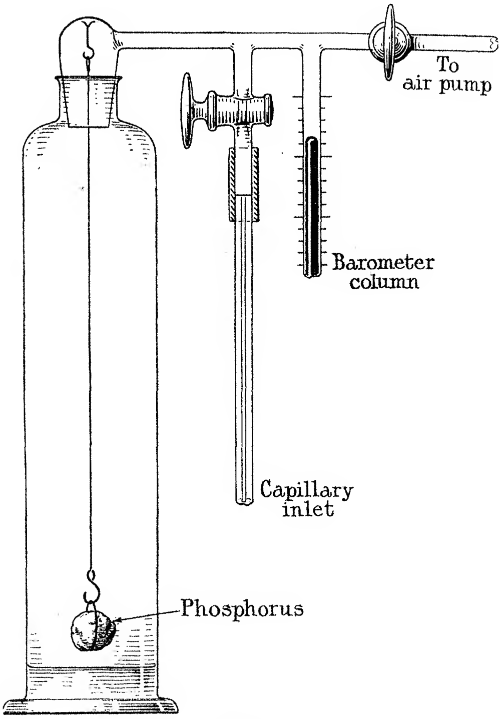

Fig. 3.

When the bottle contained a little water, intermittent luminous pulses travelled down it. Substituting strong sulphuric acid, the light at the top of the bottle, where air was diffusing into the phosphorus vapour, became quite steady. With acid of density 1·52 (vapour pressure 3 mm.), the flickering was much less conspicuous than with water only. Finally, acid of density

1·66 (vapour pressure 0·8 mm.) was about the densest that would leave any perceptible unsteadiness in the light.

The saturation pressure of phosphorus vapour at ordinary temperatures is 0·025 mm. To get the intermittent luminosity will require a pressure of water vapour about 100 times as great.

It will be seen, then, that the quantity of water vapour required is of quite a different order of magnitude from that concerned in Baker's experiments.* He found that prolonged drying over phosphorus pentoxide would stop the action of oxygen on phosphorus altogether.

§ 3. *Experiments with Camphor.*

The formation of luminous pulses evidently requires, as Joubert recognised, that combination between oxygen and phosphorus vapour should not occur until a certain concentration of oxygen is reached. At this point in the investigation it appeared clear that this restraining action was due to a peculiar action of water vapour. One could not fail to be reminded of the well known action of ethylene, oil of turpentine, and numerous other substances, organic and inorganic, which are known to inhibit the oxidation and glow of phosphorus. Their action, it is true, is far more powerful than the action of water, but it seemed likely that the difference was only one of degree: if so, a judicious use of these substances would make it possible to get the travelling pulses in a much more striking form. This expectation was eventually confirmed. The earlier experiments made with ethylene and turpentine were not successful: I pass, therefore, to those made with the vapour of camphor:—

(1) A tubular bottle of 260 c.c. capacity, about 15 cm. long and 4·5 cm. diameter, was used. At the bottom were placed a few pieces of phosphorus and a few pieces of camphor, about the size of peas.

No precaution was taken to keep the camphor and phosphorus separate, nor did this seem necessary.† The bottle was exhausted, and air allowed to leak in slowly through a capillary tube. The general arrangement was similar to that of fig. 3, though in the present case the phosphorus was not suspended. The air pressure rose at a rate of about 0·28 mm. per minute.

Five minutes after the evacuation, a brilliant pulse or flash of greenish yellow light was seen to pass down the bottle. Another similar flash passed after 1½ minutes, and after that succeeded a series of flashes. The interval between them soon settled down to a pretty regular value of about 1 minute.

If the experiment is allowed to continue with the same rate of admission of air, nitrogen accumulates in the vessel and makes diffusion less easy. At a pressure of a few centimetres it is found that the luminosity which passes down lingers on the surface of the phosphorus for a second or two, and then for longer. Finally the phosphorus remains continuously aglow, and the pulses cease.

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* 'Phil. Trans.,' 1888, p. 584.

† Though an apparent charring of the camphor was noticed after some weeks.

It is possible, however, to work in an atmosphere of nitrogen at atmospheric pressure. In this case the admission of oxygen must be slower to allow for the much longer time needed for the diffusion of phosphorus vapour away from the phosphorus surface.

The same bottle, with the phosphorus and camphor undisturbed, was filled to atmospheric pressure with nitrogen, and a capillary tube, 45 cm. long and 1 mm. diameter, attached to the neck, so as to allow of slow diffusion of atmospheric air into the bottle. This showed most striking effects. Thin and very bright pulses would start up and travel slowly along the length of the bottle. Sometimes they started in the middle, dividing into two, one of which travelled up and the other down. At other times a pulse would start from the top or from the bottom, and traverse the entire distance in one direction. These pulses were from 1 to 2 mm. thick (diameter 45 mm.) and travelled about 2 cm. per second. They contrast with the pulses observed in a rarified atmosphere (1 cm. pressure), which were 10 to 20 mm. thick, and travelled at a speed roughly estimated at 1 metre per second. The latter were much brighter, as is to be expected from the much shorter time they take to traverse the vessel, for the amount of phosphorus burnt in each case is not very different.

The thinness of the pulses at atmospheric pressure is due, no doubt, to the diminished facility of diffusion. Sometimes they were very flat, and accurately perpendicular to the axis of the cylinder in which they moved. At other times they had irregular curvature and were oblique to the direction of propagation. These differences are doubtless to be attributed to irregularities of temperature in the vessel.

In the apparatus as described, the average interval between pulses was about 8 minutes, though its action was liable to temporary disturbance by changes in the barometric height. It has remained in good order for several weeks at the time of writing, and there is no apparent reason why it should not remain so for much longer.

Some other substances give very similar results to camphor. They were tried in the exhausted bottle only. A piece of filter-paper, moistened with the liquid, was placed at the bottom, and a piece of phosphorus hung just above (as in fig. 3). The substances found to behave thus were nitrobenzene, butyl alcohol, amyl nitrite, and oil of bitter almonds—one drop only of the latter on filter paper. No doubt the list might be much extended. Ammonia may be added to it (see § 6).

§ 4. *Experiments with Pear Oil.*

A piece of filter paper was moistened with pear oil (consisting chiefly of amyl acetate), and placed at the bottom of a narrow bottle (height 18 cm., diameter 6 cm.), with a slice of phosphorus hung just above it. The bottle was exhausted, and air allowed slowly to leak in through a capillary tube. At first the phenomena were similar to those observed with camphor, but at a pressure of about 5 cm. a change occurred, the luminous pulse starting not from the top, where air was entering, but from the phosphorus surface. At the same time luminosity would cling to the phosphorus surface a second or two, after which it was extinguished. This tendency of the pulse to start from the phosphorus surface was repeatedly noticed in various experiments with pear oil under different conditions. Amyl alcohol gives the same effect. It is possible that camphor, or some of the other substances, which have been classified with it, might do the same if the right conditions were found. But they certainly do it less readily, if at all.

§ 5. *Oil of Turpentine.*

If a full quantity of this oil is placed in the bottle, luminosity is entirely stopped at all pressures up to the atmospheric. It was thought at first that a reduced quantity would probably give the brilliant luminous pulses observed with camphor, but this did not prove to be the case. When only one drop was placed on filter paper, and introduced into the bottle, there was still enough vapour to inhibit the oxidation of phosphorus at low pressures.

The one drop may still have been enough to give saturated vapour. In order to reduce the effect, turpentine was dissolved in 100 times its volume of olive oil, or (in another experiment) in the same volume of medicinal paraffin. It was then found possible, with a very slow feed of air, to get periodic luminous waves, but they were of a different character from the comparatively thin and very bright pulses obtained with, *e.g.*, camphor. The head of the luminous wave was equally definite, but it left the whole track luminous behind it for a perceptible interval, after it had reached the bottom. All then became dark again.

These experiments seem to show that turpentine is not radically different in its inhibiting action from substances like camphor. The difference that there is cannot, however, be explained as merely due to a stronger action;

for no concentration of turpentine, great or small, will give the effects as well as camphor.

The following oils, which were casually tried, seemed to behave like turpentine: aniseed, lavender, peppermint, eucalyptus, cinnamon.

§ 6. *Experiments with Ammonia.*

Ammonia gives effects like camphor. Its solubility in water, and the convenient control obtained by diluting the solution, makes it suitable for tests of how the period is controlled by the strength of the inhibiting substance, when air is admitted at a definite rate. The vessel used was a cylindrical bottle, 18 cm. long, and 6 cm. diameter. A capillary tube admitted air so as to raise the pressure 7 mm. of mercury per hour. The same capillary remained in used throughout the experiments with ammonia. A slice of phosphorus was hung up about 1 cm. above the layer of liquid at the bottom of the bottle (fig. 3).

Observations were made on the time required after evacuation for the pulses to begin, and also on the period. The latter was rather irregular at first, and somewhat longer than the steady value given, which was attained after the first few flashes had passed. Some residual irregularity remained, however, even when this comparatively steady state had been reached.

Ammonia density.	Time before first flash.	Period.
	minutes.	minutes.
[1·00*	1·1	0·033]
0·997	4·5	0·43
0·994	12·0	0·55
0·982	52·0	1·2
0·965	150·0	3·1
0·960	More than 240	4·1
0·955	Character of phenomena changed.	

* Water only.

Both the period and the time taken for the pulses to begin increase with the strength of the ammonia, but the latter time increases much more rapidly.

The time-lag before beginning measures the oxygen required to be present (1 minute = 0·023 mm. oxygen pressure), and the period measures on the same scale the oxygen consumed at each flash; for the steady *régime* implies that the oxygen consumed at each flash is the amount which leaks in during one period.

It appears, then, that the fraction of the whole stock-in-trade, so to speak, of oxygen, which is consumed at one flash diminishes when stronger ammonia is used, and the period becomes slower. With the weakest ammonia, about one-tenth of the whole amount present was consumed at each flash; with the strongest, less than one-sixtieth. It is not surprising, in the light of this, that the successive periods vary considerably in length. These periodic pulses, arising suddenly, travelling from one end of the vessel to the other, with completely dark intervals between them, are attributed to the combustion of the phosphorus vapour already present in the tube. Immediately after a pulse has passed, all the phosphorus vapour is consumed and a fresh quantity evaporates during the dark interval between the pulses.

Obviously, if this *régime* is to be followed, there is a limit to the period, under the condition of constant influx, as in the present experiments with ammonia. The period cannot be longer than the time required to admit enough oxygen to burn the whole of the saturated phosphorus vapour.

If we take the phosphorus molecule as P_4, oxidising to P_2O_5, it will combine with five times its volume, and hence with five times its partial pressure of oxygen. The careful measurements of Centnerszwer* give the vapour pressure of phosphorus vapour at 20° C. as 0·025 mm. This would require 0·125 mm. of oxygen for its complete combustion.

In the experiments with ammonia of longest period (4·1 minutes) the oxygen entering in a period is $4{\cdot}1 \times 0{\cdot}023$ mm. $=$ 0·094 m.m. This is ·75 of the amount required for complete combustion, and therefore it might be anticipated that the limiting period for simple pulses has practically been reached.

Experiment confirms this. When the ammonia concentration is increased still further it is found that the character of the *régime* changes entirely, though it still remains periodic. Thin pulses no longer travel down the vessel, and there are no longer completely dark intervals. The space round the phosphorus is filled with a diffuse luminosity, which increases periodically in brightness, but which is never reduced to zero and is not propagated through the vessel in a detached pulse right away from its place of origin. In this case the conditions which determine the period are altogether different. The quantity of phosphorus vapour burnt during a period is not limited by the saturation pressure, since the amount of evaporation while combustion is actually proceeding is no longer insensible.

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* 'Zeit. Physik. Chemie,' vol. 85, p. 99 (1913).

§ 7. *Some Unclassified Observations.*

In addition to the phenomena described above, some others have been noticed which have not been investigated in detail. Thus in the experiments with camphor, I have sometimes seen a faint glow in the vessel before the passage of the brilliant pulse and heralding the approaching catastrophe. Sometimes too a faint glow remained for a second or two after the passage of the pulse.

Placing iodine in the vessel, the phosphorus surface would under some conditions light up and become abruptly extinguished again in a curious manner. It was thought that in this case chemical combination between phosphorus and iodine introduced some complication.

§ 8. *Probable Mode of Action of Inhibiting Substances in Preventing the Oxidation of Phosphorus.*

The power possessed by a trace of ethylene or turpentine or ammonia in hindering the glow of phosphorus has always seemed very strange and difficult to explain. It is sometimes said to be an example of "negative catalysis," but this phrase is not of much help.

Although no complete account can yet be given, the present experiments seem to show in what direction the explanation lies.

Consider a luminous wave travelling through a vessel containing phosphorus, air, and some inhibiting substance. When once this wave has been started, it is propagated through the vessel. This implies that combustion in any layer is started by contact with a previous layer which is already in the act of combustion. Now why does contact with the layer already in combustion produce this effect? In the case of a mixture of oxygen and hydrogen the reply would be that the high temperature developed by combustion heats the neighbouring layer and starts that into combustion also. In the present case such an explanation is scarcely tenable, for the rise of temperature to be expected is too small. Consider the propagation in the experiment of p. 377 when the vessel was filled with nitrogen at atmospheric pressure. Let us suppose that the phosphorus vapour was saturated and that the whole of it was burnt—the least favourable supposition for the argument. Taking the vapour pressure as 0·025 mm. (Centnerszwer, *loc. cit.*) and the molecule as P_4, a litre of nitrogen contains 0·181 mgrm. of phosphorus. The complete combustion of this quantity would give 1·07 calories, and this would only heat the containing atmosphere of nitrogen 3·6°. This then is the highest temperature which could be communicated to a neighbouring layer in which combustion had not yet begun. It may well be doubted whether so small a rise could determine the propagation of combustion: but there is evidence that propagation takes place under much less favourable conditions even than this.

We have supposed that in the experiments with camphor at atmospheric pressure, the full saturation quantity of phosphorus is being burnt. In the much less brilliant and more frequent pulses obtained in presence of water vapour, the quantity burnt must be much less—at a moderate estimate, *e.g.*, five times less. But we may go further still: for in some experiments (see p. 375) the pulses obtained in presence of water vapour, faint at the best, become much fainter still as they progress, and are reduced in intensity, perhaps five times further still, before they finally die out.

In this latter case, if we take the brightness as a measure of the rate of combustion, as it appears reasonable to do, we must suppose that perhaps not more than ·04 of the saturated concentration of phosphorus vapour is being consumed. This would only give a rise of temperature of about 0·14° C., and it is still harder to believe that this would determine propagation.

If propagation is not due to rise of temperature what is it due to? I think we must attribute it to the provision of nuclei.

There is a well known experiment on supersaturation which will illustrate what is meant. A supersaturated solution of, *e.g.*, sodium acetate, is contained in a long glass tube. If a fragment of the crystallised salt is dropped in at one end, crystallisation is propagated along the tube. The crystallisation of any given layer provides nuclei which determine the crystallisation of the next layer.

Similarly, I think we must suppose that the combustion of phosphorus provides nuclei which facilitate the action. The action postulated has some analogy with the action of platinum or other solid surfaces in promoting union of hydrogen and oxygen. The gaseous or particulate products of combustion of phosphorus are assumed to act somewhat similarly.

Coming now to the inhibiting substances, I think these must be supposed that these act by taking prior possession of the nuclei, and thus making them unavailable for propagation. That water, and still more, ammonia in presence of water, would seize on the products of oxidation of phosphorus, is no more than we may anticipate from the acid-forming character of the latter. In the case of camphor or turpentine, the kind of action here assumed has become familiar in studies of the mobility of gaseous ions in air at atmospheric pressure. The ions tend to unite with gaseous molecules, as evidenced by their diminished mobility in an electric field; and this effect is highly selective. A trace of water vapour or of an organic vapour has far more tendency to load the ions than a full atmosphere of nitrogen or hydrogen.*

The original spontaneous ignition is regarded as due to something which, from a molecular point of view, is a rare accident, concerning a few molecules only. Unless it can spread and multiply, it effects practically nothing: being in this respect like a single microbe in the putrefaction of wounds. The presence of a small quantity of a vapour like oil of turpentine, by attaching itself to the product, prevents the latter from inducing the combination of the neighbouring phosphorus molecules. From this point of view, it is not specially surprising that a very small quantity of the inhibiting substance should in some cases be enough to stop the action. It is often quoted as a surprising fact that one part of ethylene in 400 parts of air inhibits the glow of phosphorus. But, after all, even at this dilution, the partial pressure of the ethylene is still about 100 times the saturation pressure of the phosphorus vapour itself. There can be little doubt that the glow of phosphorus is in all cases due to the oxidation of vapour, since the phenomenon may be traced continuously from atmospheric pressure to low pressures, and in the latter case occurs visibly at a distance from the phosphorus surface. At low pressures the vapour has a chance to diffuse away to some distance before getting oxidised.

Where, as in the periodic luminous pulses, an increasingly favourable composition of the phosphorus-oxygen mixture eventually starts a wave of combustion in spite of the inhibitor, we must suppose that the action of the inhibitor in destroying the nuclei is overwhelmed by the too rapid multiplication of the latter; just as the too rapid multiplication of invading bacteria in a wound may overwhelm the destructive action of the phagocytes and enable infection to spread.

The question may be asked why some of the inhibiting substances—like water, camphor, and ammonia—lend themselves so much more readily to the formation of intermittent luminous pulses than others, like turpentine and eucalyptus oil. As already shown, the latter class can be made to give the effect by dilution, but not so well.

Striking as the difference is, it is probably not very fundamental—not perhaps more fundamental than the condition of "hunting" or not hunting in a self-regulating mechanism, such as a steam engine governor or an automatic arc lamp.

In these cases a general explanation of the action of the mechanism is by no means sufficient to determine whether it will "hunt" or not. Nor can the provisional theory of the action of inhibiting substances which has been given be expected to do so.

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* To avoid misconception it is well to state specifically that I do not assume that the ions produced in the oxidation of phosphorus have necessarily anything to do with the matter.

§ 9. *Summary.*

The paper deals with the intermittent or periodic luminosity observed to be propagated through the gas space when the last traces of oxygen are being removed from air by means of phosphorus, or when air is allowed slowly to leak into an exhausted vessel containing phosphorus.

(1) It is shown that this effect, as ordinarily observed, requires the presence of water vapour. Moderate drying (*e.g.*, by sulphuric acid) makes the glow perfectly steady. Water vapour has therefore the power of inhibiting the combination of phosphorus vapour and oxygen within certain limits. When the composition of the mixture becomes favourable beyond those limits, a wave of combustion is propagated.

(2) Other substances are known to inhibit the glow of phosphorus. Some of these can be used to exhibit the above phenomena in a far more striking form than water. Camphor, ammonia, and pear oil are among the most effective, and experiments with them are described in detail.

(3) It is shown that the propagation of these waves of combustion cannot be attributed to the rise of temperature of one layer igniting the next layer, for the rise of temperature is too small. An alternative theory of the propagation is proposed, which assumes that it depends on the provision of nuclei, as in the propagation of crystallisation through a super-cooled liquid.

(4) On this basis a theory of the action of the inhibitors (sometimes called "negative catalysts") is developed.